PCT/NZ2004/000305

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CERTIFICATE

This certificate is issued in support of an application for Patent registration in a country outside New Zealand pursuant to the Patents Act 1953 and the Regulations thereunder.

I hereby certify that annexed is a true copy of the Provisional Specification as filed on 27 November 2003 with an application for Letters Patent number 529803 made by Blue Marble Polymers Limited.

Dated 13 December 2004.

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529803

Patents Act 1953

PROVISIONAL SPECIFICATION

Method and Apparatus for Producing Bio-Degradable Foam

We, Blue Marble Polymers Ltd, 61 Wickham Street, Christchurch, New Zealand, a New Zealand Company do hereby declare this invention to be described in the following statement:

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METHOD AND APPARATUS FOR PRODUCING BIO-DEGRADABLE FOAM

TECHNICAL FIELD

The present invention relates to a pressurised microwave apparatus used for producing foamed articles from resins, especially bio-degradable resins.
The present invention further relates to improvements in a process for forming bio-degradable foamed articles using a combination of microwave and pressure, and the bio-degradable foamed articles formed thereof.

BACKGROUND ART

The present invention builds on the inventions disclosed in PCT/NZ/0100052 and PCT/NZ/0200226. In PCT/NZ/0100052 a two stage process is described for producing a bio-degradable foamed product with improved packaging properties including resilience, compressibility and shock absorption. In PCT/NZ/00226 a process is described for producing improved foam surface finish by causing the inner mould surface to heat to a predetermined temperature during processing and the use of a multiple magnetron microwave oven for heating. Definitions used in these applications are included by reference herein.

The area of bio-degradable packaging is widely discussed in the prior art. A variety of products exist that attempt to produce bio-degradable foamed materials as discussed in patent applications PCT/NZ/0100052 and PCT/NZ/0200226.

A number of processes have been employed to produce thick-walled bio-degradable foams suitable for packaging applications, including direct extrusion methods, conductive heating methods, pressurised vessel methods and volumetric heating methods such as microwave heating.

Bio-degradable moulded foam shapes produced by microwave heating

This invention builds on the products and processes disclosed in PCT/NZ/0100052 (Blue Marble) and PCT/NZ/0200226 (Blue Marble). Such starch-based foam shapes formed by microwave heating have the attributes of up to one metre wall thickness and a finished surface appearance achieved by elevating the mould wall temperature during processing. A multiple magnetron oven design is described and although pressure and rapid depressurisation means are contemplated in conjunction with microwave heating, neither processing sequences using pressure nor an apparatus design encompassing pressure and depressurisation functions are disclosed.

WO98/51466 (ATO) details a process for forming thick-walled bio-degradable foam using a single step microwave heating process. They found that it was important for the foaming process to proceed rapidly by either using a microwave source having a high output or by a combination of a microwave generator and a mould, in which the pressure could be varied rapidly. However no pressure ranges or heating sequences are detailed, nor is there any description of a microwave and pressure capable apparatus. In the examples cited a 60 second cycle time is required to produce a foam with a density of 150-160kg/m^3.

EP1347008 (Novamont) discloses a process for preparing foamed articles of bio-degradable plastic material. Foaming particles prior to bonding and bonding of particles utilising microwave heating are contemplated, however no detail of any apparatus or any heating profile is provided and further the examples do not describe microwave heating.

Microwave Oven Designs for moulded foam shapes

US4908486 (Nearctic) discloses a multiple magnetron microwave cavity designed for drying products. While disclosing the principles behind a multiple magnetron design to improve field uniformity the apparatus is designed for drying applications and does not anticipate the issues associated with combining cavity or mould pressurisation / depressurisation in conjunction with rapid microwave heating or of producing foamed articles.

US4298324 (Isobox-Barbier) discloses a microwave and mold design for expanding plastic resins. The cavity splits in half with one half remaining fixed and the other moving to allow ejection of the foam shape. Bio-degradable resins are not contemplated, nor are multiple magnetron cavity designs or pressure profiles.

Microwave and Pressure combination designs for moulded foam shapes

WO02/20238 (ATO) details a process for manufacturing thick-walled bio-degradable foamed articles involving a rapid, discontinuous or semi-continuous process of subjecting a biopolymer to elevated temperature and pressure in a closed-off space,

maintaining this situation for a certain period of time and followed by a rapid depressurisation causing the biopolymer to foam. Although microwave and pressure combinations are contemplated they are not demonstrated and the only example cited utilises steam to achieve the elevated temperature and pressure profile, with a heating cycle time of 5 minutes. Such a long cycle time is not economic and therefore a process and apparatus capable of reducing the heating cycle time to less than one minute is more desirable.

WO90/08642 (Adfoam) discloses an apparatus design and process for producing foamed plastic articles. The apparatus disclosed utilises 5kW magnetrons which are exponentially more expensive than standard domestic magnetrons and requires that the mould is moved within the cavity during processing to achieve a uniform microwave field. Depressurisation rates in conjunction with elevated pressure and microwave heating are not contemplated, nor are bio-degradable resins.

According to the methods known from prior art there is a tradeoff between foam density, heating cycle time and apparatus cost. Prior art does not recognise the significance of the combination of the process parameters and that without them a low-density foam with an adequate surface finish cannot be produced in a cycle time of less than one minute.

Therefore there is a need for a method and apparatus that allows the production of low-density bio-degradable foams with adequate mechanical properties at a microwave and pressure heating cycle time of less than one minute

It is an object of the present invention to at least provide the public with a useful choice.

Further aspects and advantages of the present invention will become apparent from the ensuing description and drawings, which are given by way of example only.

DISCLOSURE OF INVENTION

For the purposes of this invention, heating cycle is defined as a cycle that commences when the material for foaming is situated inside the closed mould and is ready for processing into a foam, and ends when the resultant foam is ready for ejection from the mould. Materials handling procedures are not included in the heating cycle time.

According to one aspect of the present invention there is provided a method for producing a bio-degradable foamed product, said method including the steps of:

a) placing a bio-degradable starting material in a mould, wherein the starting material has been processed into a form ready for foaming;
b) positioning the mould and starting material in a microwave cavity;
c) subjecting the mould and starting material to microwave heating before, during or after elevating pressure;
d) subjecting the mould and starting material to depressurisation during or after microwave heating;
e) ejecting the foam from the mould;

characterised in that the foam has a final density of between 10 and 200kg/m^3.

Preferably the entire heating cycle time is less than one minute.

According to a further aspect of the present invention there is provided a bio-degradable foam product with qualities including a density from 10 to 200kg/m^3; a soft, resilient and continuous foam surface; a wall thickness of up to 1 metre produced by the method including:

a) placing a bio-degradable starting material in a mould, wherein the starting material has been processed into a form ready for foaming;
b) positioning the mould and starting material in a microwave cavity;
c) subjecting the mould and starting material to microwave heating before, during or after elevating pressure;
d) subjecting the mould and starting material to depressurisation during or after microwave heating
e) ejecting the foam from the mould;

By controlling the pressure, heating, timing of depressurisation, and rate of depressurisation, the level of expansion can be balanced against the level of shrinkage and hence the foam can be produced at a reduced density in a cycle time of less than one minute.

The preferred starting material is that described in PCT/NZ/0100052 and PCT/NZ/0200226. It is desirable that the starting materials are bio-degradable and thus offer a significant environmental benefit over traditional materials such as polystyrene, however any starting material which behaves in the same manner during such a heating and pressure cycle is incorporated herein.

More preferably the starting material is in the form of extruded pellets or particles formed by communition.

The starting material may be pre-heated prior to the pressurised heating step being initiated.

The preferred mould arrangement is that described in PCT/NZ/0200226 where a largely microwave transparent mould material is coated with a susceptor to cause the inner mould surface to heat to a predetermined temperature range during microwave heating.

Preferably the mould is vented on all walls

Preferably the cavity or outer mould is pressurised to between 1.5 and 100 bar prior to processing

More preferably the cavity or mould is pressurised to between 3 and 20 bar.

Preferably the pressure can be altered at any time during the heating cycle.
Where pressures in excess of 20 bar are used, additional design considerations are required and therefore a rate of heating and pressure mix which balances the cost of microwave heating capacity and the cost of pressure design will minimize the cost of a system and the process cycle time.

Unexpectedly the rate of depressurisation can also significantly impact the level of initial expansion and final foam density. Too high a rate of depressurisation results in excellent initial expansion but a high level of shrinkage, whereas too slow a rate of depressurisation doesn't allow adequate initial expansion.

Thus there appears to be an optimum rate of depressurisation where the net effect of expansion and shrinkage yields a foam of the lowest density and the best surface appearance.

This optimum rate can be achieved by matching the rate of depressurisation to the temperature profile for a particular starting material.

Preferably the rate of depressurisation of the cavity or mould during heating is between 0.001 and 200 bar per second

More preferably the time for full depressurisation to be completed is between 0.01 and 10 seconds.

It was found that up to a point the greater the time until the depressurisation is initiated, the greater the level of expansion. If the heating time before depressurisation is too short, insufficient time has occurred to allow initiation of boiling of the water contained in the pellets, and hence no or little expansion will result from the large depressurisation.

Where the depressurisation is initiated early in the processing sequence the pellets showed signs of having ruptured untimely during depressurisation. This is the result

of subjecting the pellets to explosive decompression before the pellets had heated sufficiently to plasticise the pellets to a point where they would flow rather than rupturing immediately as the result of the expansion force of the internal vapour pressure.

It was further found that the period of time heating is continued after the depressurisation is initiated is also critical to the final foam properties. Where processing time after the depressurisation is too short significant shrinkage results, where it is too long, overcooking of the foam results.

The explanation for these observations is thought to be that too long a heating time before initiating depressurisation results in the internal vapour pressure inside the pellets being significantly greater than the pressure in the vessel. If the vapour pressure inside the pellets is greater than the pressure in the vessel vapour from the pellets would be able to escape thus drying the pellets out and leaving them vulnerable to overcooking.

Further, by controlling the timing of the depressurisation and the rate of depressurisation, untimely rupture of the pellets can be avoided and the final density of the foam can be reduced.

In an alternative embodiment vacuum can be used to generate the pressure drop, given it is the pressure change that is important, not whether it is derived from a positive or negative pressure base.

In order to obtain a fully moulded product with a continuous soft resilient foam surface a high enough moulding pressure is required. Increasing the internal vapour pressure of the pellets can increase the moulding pressure. Significant improvements can be achieved by increasing the pressure of the mould or cavity surrounding the material during heating by elevated pressure increases of as little as 2.5 bar.

By using elevated pressure, the electric field strength that can be sustained without the occurrence of voltage breakdown (arcing and plasma formation) can be greatly increased. Thus the heating time can be reduced.

Elevating pressure also causes the boiling point of the water (blowing agent) contained inside the starting material to be elevated. Therefore greater vapour pressures can be reached inside the pellet before the water "flashes". The greater vapour pressure means the magnitude of the pressure drop experienced by the water vapour can be increased which in turn increases the expansion and hence lowers the density of the foam.

Further, elevating pressure and thus the boiling point of the water contained inside the starting material enables the temperature reached by the starting material to be elevated therefore reducing the viscosity of the melt and in turn increasing the expansion ratio and decreasing the density of the foam.

There is however an upper limit regarding the melt viscosity. If the viscosity is too high it may reach a point where it causes the starting material to shrink back excessively after initial expansion thus increasing the final foam density.

A further advantage of elevating pressure is that the rate of vapour loss by diffusion can be reduced and hence more energy can be delivered to the starting material, without the loss of the blowing agent (water) or burning, resulting in an increase of vapour pressure within the starting material and therefore reduced foam density. If water is the sole blowing agent, loss of vapour has a significant negative impact on both expansion and adhesion where starch-based pellets are used as the starting material.

According to a further aspect of the present invention there is provided a bio-degradable foam product with qualities of a density from 20 to 100kg/m^3; a soft, resilient and continuous foam surface; a wall thickness of up to one metre.

Preferably the above foam is manufactured using the method described above.

More preferably the foam density lies between 25 and 50kg/m^3.

By carefully controlling the pressure, heating and depressurisation profile the density, cushioning performance and surface abrasion characteristics can be controlled.

The temperature of the inner mould surface is heated to a predetermined range before depressurisation to aid melt flow. This is achieved by coating the largely microwave-transparent mould with a microwave absorbent material which will heat at the surface only when microwave energy is applied. Melt flow before depressurisation aids achievement of a continuous surface appearance.

Cushioning performance is affected by factors including voids contained within the foam, and the resilience of the surface of the foam. By controlling the pressure and depressurisation profile during heating internal mould pressure can be optimised to minimise the number of voids within the foam.

Continued heating after depressurisation minimises shrinkage and 'sets' the foam by driving further water from the material. Reducing the water level increases the viscosity of the melt to a level where it will not flow and hence cannot shrink. Eventually, the reduction in water level causes the melt to revert to a solid and hence the foam is 'set'.

Cushioning factor may be measured by a number of techniques including that outlined in British Standard BS7539. In order to protect articles with a fragility factor of between 15 and 115 it is desirable for the foam to have a G-value in a similar range. G-value for a foam is understood to give a foam with the ability to sufficiently attenuate shock and vibrations such that the packaged article under normal circumstances is unlikely to be exposed to a G-force greater than this numerical value. The higher the foam G-value the less suitable it might be for packaging fragile or delicate articles. Given the method described above a foam can be produced with a G-value to adequately protect items with a fragility factor between 15 and 115.

Foam surface characteristics can be described by way of an abrasion test. In tests carried out on the foam samples abrasion was tested by rubbing foam across aluminium sheets of differing hardness values. 30 seconds of rubbing back and forth on the bright side of an aluminium surface is sufficient to test the abrasion

characteristics of a foam. No difference in abrasion level was found when samples of expanded polystyrene were compared with samples of bio-degradable foam produced using the method described above.

According to another aspect of the current invention there is provided a pressurized microwave apparatus for carrying out the processing of the bio-degradable starting material into a finished foam, said apparatus including:

a) a microwave cavity
b) an arrangement to seal the cavity from microwave leakage and to enable the cavity to be pressurized
c) at least one inlet and one outlet port arranged around the cavity for pressurising and depressurizing the cavity
d) a mould arrangement

characterised in that the foam produced has a density of between 10 and $200kg/m^3$.

According to a further aspect of the current invention there is provided a pressurized microwave apparatus for carrying out the processing of the bio-degradable starting material into a finished foam, said apparatus including:

a) a microwave cavity
b) an arrangement to seal the cavity from microwave leakage
c) a pressurized vessel fabricated of largely microwave transparent material housed within the microwave cavity
d) a mould arrangement
e) a means for conveying the mould and or foam into and out of the pressure vessel

f) at least one inlet and one outlet port arranged around the pressure vessel for pressurizing and depressurizing the vessel

characterised in that the foam produced has a density of between 10 and 200kg/m^3.

Preferably the microwave energy density level, the pressure level and rate of depressurisation can be varied at any time during operation of the apparatus to produce a foam with the characteristics as described by the method above.

The foam produced by the apparatus has the characteristics of density, cushioning performance and surface abrasion characteristics described above.

The cavity shape may be one of a number of shapes including cylindrical, asymetrical hexagonal or semi-elliptical and may be split into two halves. Multiple wave-guide ports can be situated in each part of the cavity. Wave-guides connect the power modules to the microwave cavity via the wave-guide ports.

To seal and protect the microwave modules it is necessary to fit a pressure window between the waveguide exit and the cavity. Pressure windows are manufactured from a substantially microwave transparent material such as quartz or teflon. However as this material is expensive an alternative option is to place a thin sacrificial window made from mica, a relatively inexpensive material, in front of the window at the waveguide exit. The advantage of such an arrangement is, should any arcing or plasma occur it will damage the sacrificial mica window therefore protecting the more expensive pressure window.

Another function of the arrangement is to protect the microwave modules by utilising a pressure relief valve piped to an air space encapsulated between two pressure windows. If the pressure in this space were to exceed a pre-determined level the relief valve would open and vent the pressure to a safe location, thereby protecting the microwave modules.

Preferably one half of the microwave cavity is capable of movement in the vertical direction. This vertical movement allows opening and closing of the microwave cavity simultaneously with unclamping/clamping and opening/closing of the mould.

The microwave cavity also serves as a pressure vessel allowing the pressure at which the process is carried out to be elevated and controlled.

Preferably a ring or hoop mechanism is used to seal both pressure and microwaves within the cavity.

Preferably each half of the cavity has a castellated flange. A castellated locking ring is then rotated or clamped to seal to the required system pressure by means known in the art. Chokes are also added to the inner cavity surface where the cavity halves join to eliminate microwave leakage.

Preferably interlock devices are included to ensure that the apparatus cannot be operated without adequate sealing of the cavity.

Optionally structures such as microwave transparent platens are included inside the cavity to house the mould arrangement.

Such structures are mounted in each of the cavity halves. The two mould halves are mounted on the upper and lower support structures respectively.

Single or multiple inlet and outlet ports can be used.

Multiple inlet ports can be used to minimise the time required to pressurise the vessel to the desired pressure level without increasing the size of ports to a point where they interfere with the magnetron wave-guide arrangement.

Multiple outlet ports can be situated throughout the microwave cavity to enable depressurisation to be effected. A plurality of ports may be used to vary the rate of depressurisation. Alternatively, the rate of depressurisation may be varied using a flow-restricting device.

Compressed air may be made available to the platens and mould halves whereby compressed air is blown through the vent holes in the mould to cause the foam to be ejected from the mould.

Alternatively, injector guns (to allow loading of pellets) are connected to ports in the movable half of the mould. The injector guns are connected to feed hoppers outside the microwave cavity. The injector guns also house ejector pins. After loading of the pellets, ejector pins are positioned flush with the inner mould surface to plug the mould ports. Ejection of the foam is achieved when the ejector pins are pushed proud of the inner mould surface. Additional ejector pins may be located in the lower half of the mould.

In an alternative embodiment the cavity is equipped with a door through which the finished foam can be removed from the microwave unit. The mould can be unclamped and opened, and closed and clamped independently of the microwave cavity opening operation.

In a preferred embodiment the cavity is a multiple magnetron cavity.

The preferred mould configuration for use in the heating apparatus is that described in PCT/NZ/0200226.

In a preferred embodiments the apparatus utilizes multiple domestic magnetrons all concentrated on a cavity containing the material to be foamed and the mould as referenced above.

The number and sequence of magnetrons turned on and off during the processing can be varied to further aid uniform heating within the material being foamed. The preferred rate of heating within the material being heated is 0-25C per second temperature rise.

The preferred frequency of operation of the microwave is from 915MHz to 5GHz. More preferably one single frequency is used during processing. More preferably, the frequency used is 2450MHz.

The importance of uniformity of the microwave field throughout the processing is critical to achieving uniformity in the final foam. Microwave heating has been

inherently non-uniform due the hot and cold spots generated by standing waves canceling out and doubling field intensity where they intersect.
If the material to be foamed is not heated to and through the flash point uniformly then non-uniformities will result in the final foam.

In some designs this has been sought to be overcome by introducing a mode stirrer into the cavity, or by moving the product being heated around the cavity during processing. With a multiple magnetron design it is not necessary to add mode stirrers or move the product during heating. Additionally field patterns can be changed during heating by switching individual magnetrons on and off to further improve field uniformity.

It has been discovered that by utilizing a plurality of magnetrons situated around the walls of the cavity that a uniform field can be established within a pressurized cavity.

A further advantage of the above described apparatus is the size of workpiece that can be processed in a pressurised microwave environment. While autoclaves and microwave pressure vessels exist for uses such as chemical analysis, only very small sample sizes can be processed. The use of multiple magnetrons, pressure and microwave leakage seals, microwave transparent high performance plastics as described above allow biodegradable foam up to one metre thick to be produced in a low cost apparatus with a reduced cycle time.

BRIEF DESCRIPTION OF DRAWINGS

This invention may also be said to broadly consist in the parts, elements and features referred to or indicated in the specification of the application, individually or collectively, and any or all combinations of any two or more of said parts, elements or features which have known equivalents in the art to which this invention relates, such known equivalents are deemed to be incorporated herein as if individually set forth.

Further aspects of the present invention will become apparent from the following description, which is given by way of example only and with reference to the accompanying drawings in which:

Figure 1 is (a sectional view of a pressure vessel within a microwave cavity)

Figure 2 is (a sectional view of a pressurised microwave cavity)

Figure 3 is (a sectional view of a pressure window for a microwave wave-guide port)

BEST MODES FOR CARRYING OUT THE INVENTION

Apparatus

Referring to Figure 1; the apparatus consists of a multiple magnetron microwave cavity 1 with multiple microwave wave-guide ports 9 situated throughout the cavity walls. A vented mould arrangement 3 is filled with the required quantity of starting material (not shown) and placed within a pressure vessel of microwave transparent material 2 within the microwave cavity 1. Pressure is applied to the pressure vessel through an inlet valve 8 and released through a depressurisation valve 6 as required. The depressurised air is vented into a depressurisation chamber 7 to dissipate noise

and pressure. A safety relief valve 5 vents if pressure exceeds the maximum targeted pressure. A choke system 4 is situated at the junction of the pressure vessel 2 and the microwave cavity 1 to prevent leakage of microwaves during processing.

Referring to Figure 2, an alternative embodiment; the apparatus consists of a microwave cavity which also serves as a pressure vessel 10,11. A microwave choke 12 prevents leakage of microwaves from the cavity 10,11. A locking mechanism 13 clamps the cavity halves 10,11. Mould halves 17 are clamped simultaneously. Locator pins (not shown) ensure the mould 17 and cavity halves 10,11 are aligned correctly. Microwave wave-guide ports 14 are situated throughout the cavity walls 10,11 and are positioned to minimise cross-coupling of microwaves during operation. Inlet ports 15 enable the entire cavity 10,11 to be pressurised. Outlet ports 16 are used to depressurise the cavity 10,11. A depressurisation chamber (not shown) is used to dissipate noise and pressure generated by the depressurisation process. Support structures 18 brace the mould against the cavity walls 10,11.

Referring to Figure 3; Each wave-guide port 14 (see Figure 2) has a sacrificial window 19 at the interface of the cavity wall through which microwaves enter the cavity. Behind the sacrificial window are further pressure windows 20 separated by an air pocket 22 with a safety relief valve 23. The valve vents if pressure reaches unsafe levels, thus protecting the microwave modules (not shown) attached to the wave-guides.

Mould

The mould material used is ULTEM polyetherimide, the inner mould surfaces are coated with a ferrite/silicone rubber liner which acts as a susceptor to allow the surface of the mould to heat to a predetermined temperature during microwave heating. The mould shape is cylindrical D = 105mm, L = 255mm. The mould is vented on all walls.

For a discussion on suitable mould materials and mould configurations refer to PCT/NZ/0200226.

Procedure

1) 110g of starch pellets at around 22% moisture were placed in the mould
2) The mould was clamped shut
3) The mould was placed inside an ULTEM pressure vessel inside the microwave cavity
4) The pressure vessel was sealed and the microwave cavity closed
5) The power level was set to maximum power of 16 magnetrons arranged around the the microwave cavity
6) The process time was set to t=30 seconds
7) The pressure vessel (and mould contained within) was pressurised to 10 bar over a period of 5 seconds
8) Microwave heating was initiated
9) At t=22 seconds the pressure vessel was depressurised to atmospheric pressure via a ½ inch valve, taking approximately 5 seconds to return to atmospheric pressure
10) At t=30 seconds the microwave heating was stopped

Result

A fully formed foam shape with a density of $42kg/m^3$ and a smooth and resilient foam surface was obtained.

Aspects of the present invention have been described by way of example only and it should be appreciated that modifications and additions may be made thereto without departing from the scope thereof.

Dated this 27th Day of November 2003

BLUE MARBLE POLYMERS LIMITED

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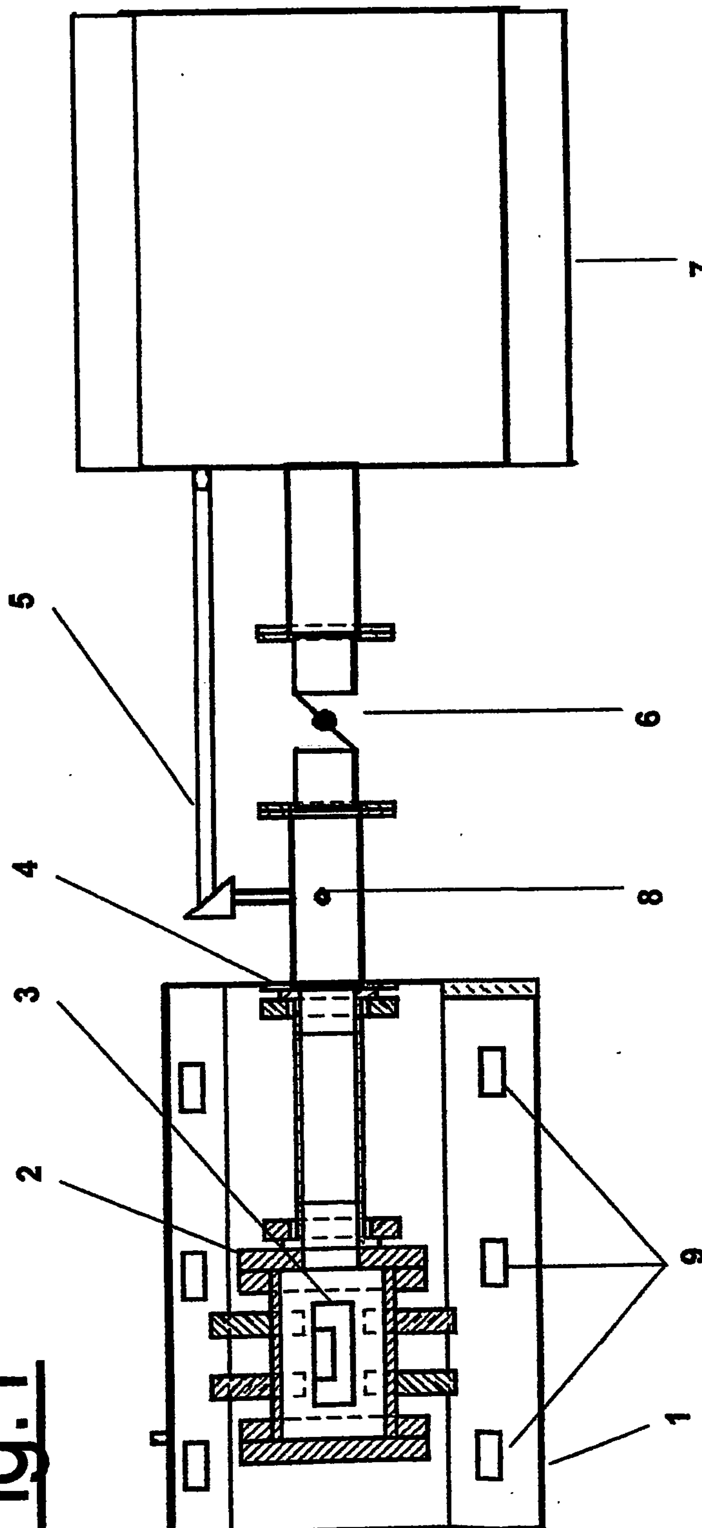

Fig.1

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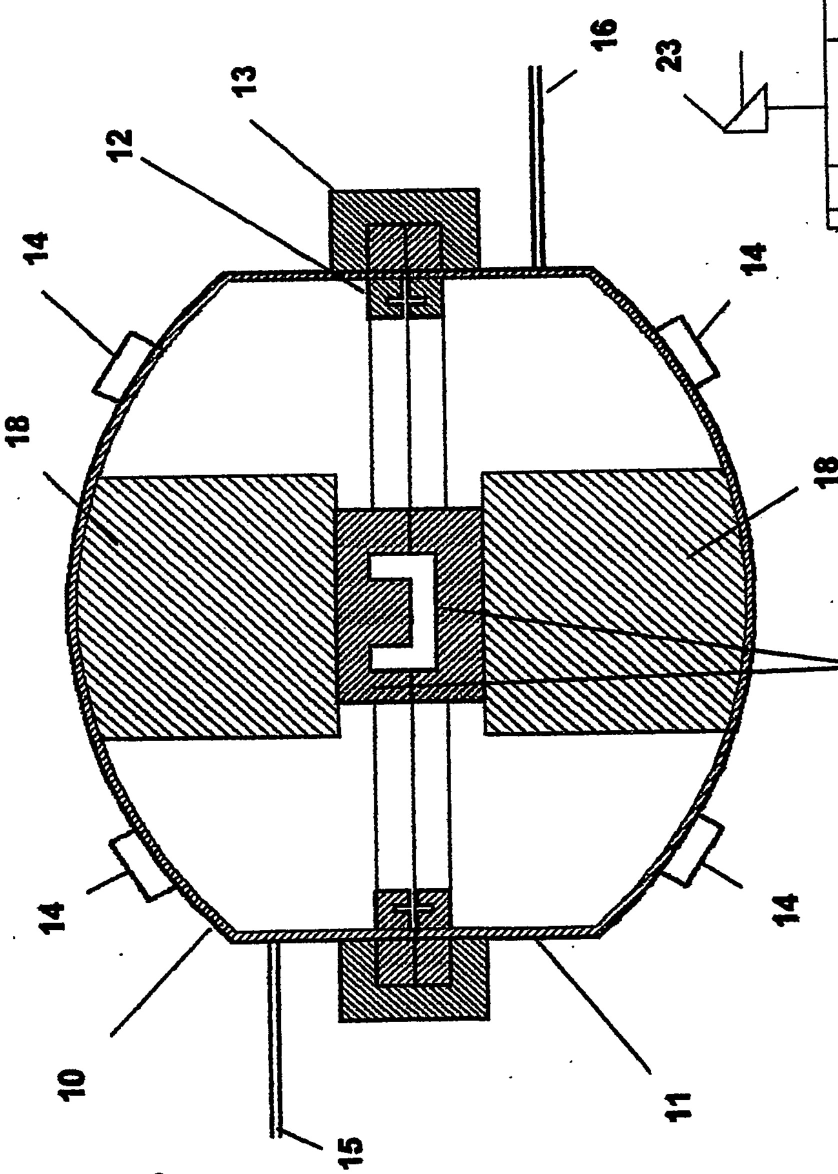

Fig.2

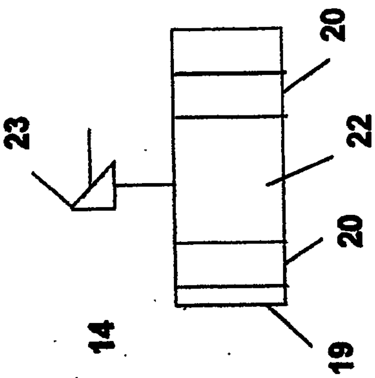

Fig.3

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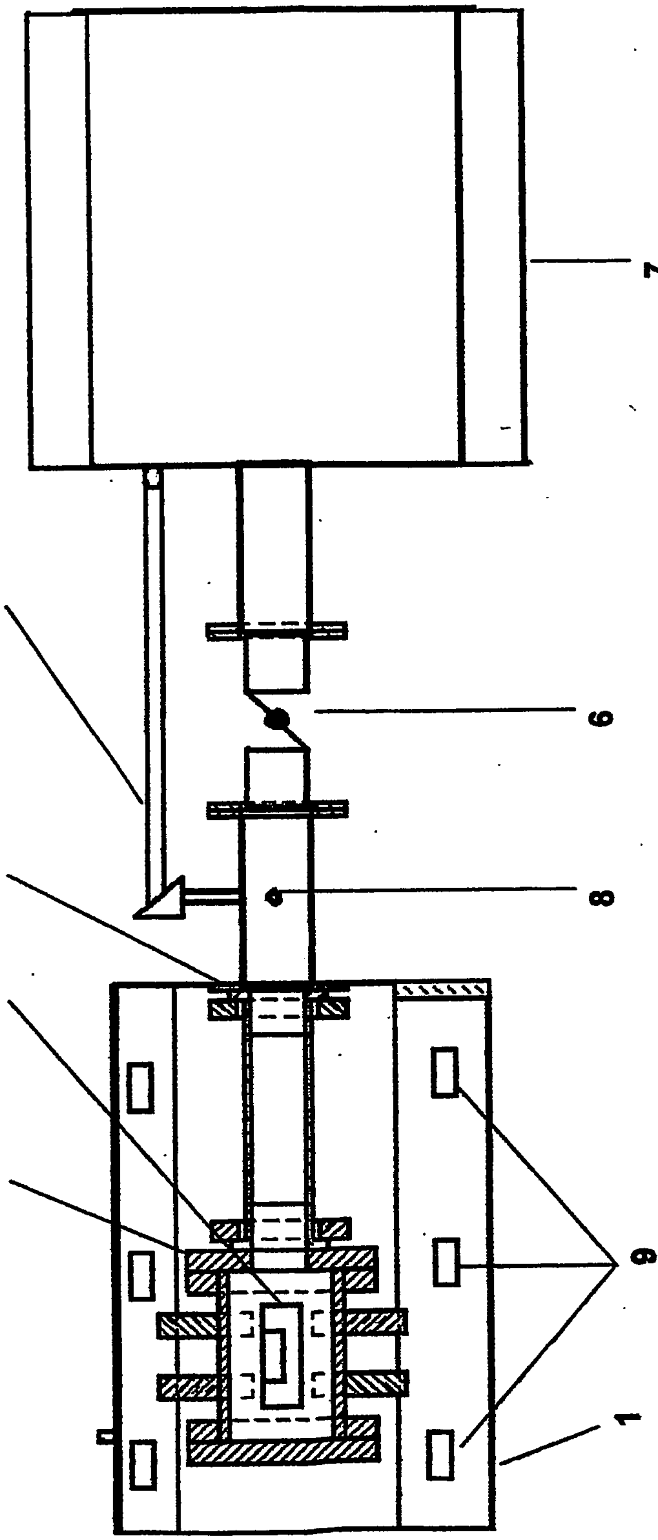

Fig.1

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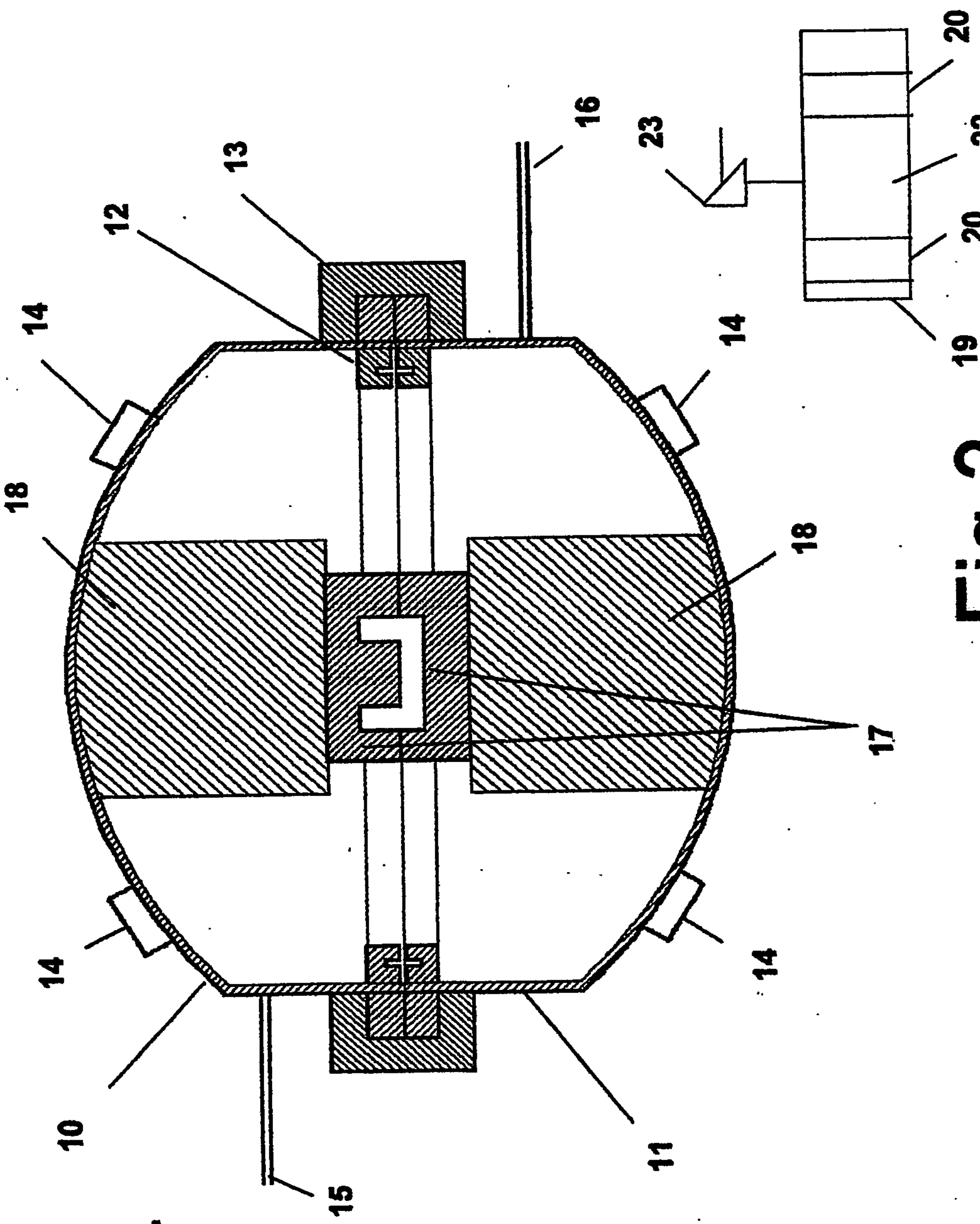

Fig.2

Fig.3

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